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LILIOSIDE A AND B, TWO NEW GLYCEROL GLUCOSIDES ISOLATED FROM LILIUM LONGIFLORUM THUNB.

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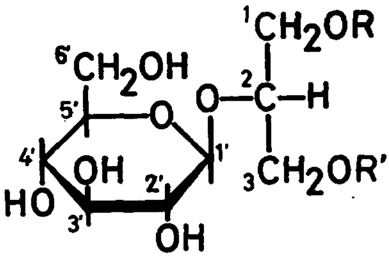
In the course of our studies on the constituents of Liliaceae plants, we have now isolated two new glycerol glucosides, named lilioside A (I) and B (II), from a popular lily, Lilium longiflorum Thunb. (Japanese name: teppō-yuri).

80% aqueous MeOH extract of the fresh leaves and stems of the plant was washed with $CHCl_3$ and the water layer was concentrated and placed on a carbon-Celite (1:1) column. The column was first washed with water to remove monosaccharides and then eluted with EtOH-water mixture with successive increasing of EtOH concentration (2.5%, 5% and 10%). Each fraction was examined by TLC and GLC. 10% EtOH fraction gave lilioside A (I), colorless prisms, $C_{11}H_{20}O_9$, mp 146-148°(from EtOH), $[\alpha]_D^{23}$ -21.8° (H_2O). 5% EtOH fraction, which was shown to be a mixture of lilioside B and sucrose, was further separated on a silica gel column using $CHCl_3$-MeOH (4:1) mixture as the solvent to yield lilioside B (II), colorless needles, $C_9H_{18}O_8$, mp 166-167°(from EtOH), $[\alpha]_D^{26}$ -30.2°(H_2O). The yields of lilioside



I : R = Ac , R' = H
or R = H , R' = Ac

II : R = R' = H

A and B from the fresh leaves and stems were about 0.6% and 0.1%, respectively.[1]

The spectral data of lilioside A and B were very similar and suggestive of glycoside structures of the same type. Lilioside A, however, gave the IR absorption bands at 1725, 1250 cm^{-1} (KBr) and one acetyl signal at δ 2.0 (C_5D_5N) in its NMR spectrum, while lilioside B showed no such spectral features. These data indicate the presence of one acetoxyl group in lilioside A alone.

When treated with hot 5% H_2SO_4, both lilioside A and B were hydrolyzed to afford D-glucose and glycerol in equimolar ratio.

Lilioside A was acetylated with Ac_2O and pyridine to give colorless needles of lilioside A pentaacetate, $C_{21}H_{30}O_{14}$, mp 128° (from EtOH), $[\alpha]_D^{18}$ -15.5°($CHCl_3$); IR (KBr) 1750, 1240 and 1220 cm^{-1} ; NMR ($CDCl_3$) δ 2.01-2.60 (6 x OAc), 3.60-3.81 (1H,m, $C_{5'}$-H), 4.02-4.38 (7H, $C_{6'}$-H_2 , two methylenes and one methyne of the glycerol moiety), 4.62 (1H,d, J=8 Hz, anomeric H) and 4.82-5.33 (3H, $C_{2',-4'}$-H). Acetylation of lilioside B with Ac_2O and pyridine gave lilioside B hexaacetate, which was proved to be identical with lilioside A pentaacetate by mixed fusion and comparison of IR spectra (KBr) and thin-layer chromatograms. From the above results, it is shown that lilioside B is a glycerol glucoside and lilioside A is a monoacetate of lilioside B.

In a periodate oxidation study, lilioside B consumed two moles of oxidant and produced one mole of formic acid. No formaldehyde was detected in the reaction mixture. These data are consistent only with 2-O-glucopyranosyl-glycerol structure.

On enzymatic hydrolysis with emulsin, lilioside B yielded D-glucose and glycerol, whereas lilioside A afforded D-glucose and glycerol monoacetate. This observation proves that the acetyl group of lilioside A is located on the glycerol moiety, namely, at one of the two primary alcohols, and that the glucoside bonds of lilioside A and B are both β -linkage. The coupling constants of the doublet signals at δ 5.12 (J=7 Hz) and δ 5.20 (J=7 Hz) ,

(both in C_5D_5N), respectively assignable to the anomeric protons of lilioside A and B, also corroborate the β-glucoside linkage.

Consequently, lilioside A and lilioside B are now formulated as 1-O-acetyl-2-O-β-D-glucopyranosylglycerol and 2-O-β-D-glucopyranosylglycerol, respectively.[2]

Further confirmation of the structure of lilioside B was obtained by direct comparison with synthetic 2-O-β-D-glucopyranosylglycerol prepared from cellobiose according to the method of Charlson and Perlin.[3]

The absolute configuration of the glycerol moiety of lilioside A, namely, whether the acetyl group is attached to C_1-OH or C_3-OH of *sn*-glycerol[4], is not yet determined and is now under investigation.

Except glycolipids such as glycosyl diglycerides[6], only from the red algae some glycerol glycosides have so far been isolated and their sugar moieties consist of only galactose and mannose.[12,13,14] It is noteworthy, therefore, that, except glycolipids, lilioside A and B are the first examples of naturally occurring glycerol glucosides and further, the first instances of glycerol glycosides isolated from higher plants.

Further studies on the isolation of other new glycerol glycosides from some *Lilium* species are being performed in our laboratory and will be reported in the near future.

REFERENCES

1. Lilioside A and B are also found in flowers and underground parts of the plant.
2. Lilioside B is not an artefact formed from lilioside A during the isolation, because the isolation procedures were carried out under so mild conditions that lilioside A could not possibly undergo deacetylation. The presence of lilioside B along with lilioside A in the crude extract of the plant is clearly demonstrated by TLC and GLC.

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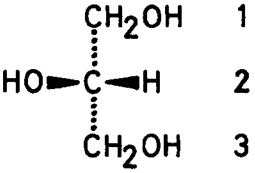
4. In order to designate the stereochemistry of glycerol derivatives, the carbon atoms of glycerol are numbered stereospecifically as shown below on the basis of the Hirschmann proposal.[5] To differentiate such numbering from conventional numbering conveying no steric information, the prefix "*sn*" is used.



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6. Glycolipids such as glycosyl diglycerides, which are also glycerol glycosides but existing esterified with fatty acids in their glycerol moieties, have been shown to be widely distributed in plants[7,8,9] and in microorganisms.[10,11]
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